# Preparation and Characterization of Electroactive Biopolymers

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**Summary:** Biopolymers have the potential for use as a matrix for applications such as controlled release devices, environmentally sensitive membranes, mimic materials and energetic applications. Renewable resources (such as starch) can be utilized as polymer matrices for electroactive materials that are sensitive to their environment. Natural polymers are generally more environmentally-friendly and biocompatible than existing synthetic products. Thermoplastic starch is naturally insulative; however, the chemical, electrical, and mechanical properties of the biopolymer matrix can be tailored for specific functionality in a continuous process utilizing reactive extrusion. Conductance can be measured in the solid state by a direct-current resistance method. Ion-conducting materials, produced by doping thermoplastic starch and biopolymers with metal halides, have 5 orders of magnitude greater conductance than native materials. There is a correlation between polymer mobility and conductance. Plant or microbial biopolymers with ionic functional groups have shown promise for higher levels of conductance. The conductance approaches the level of synthetic polymer electrolytes.

**Keywords:** electroactive biomaterials; polysaccharides; resistivity; solid polymer electrolyte; starch

## Introduction

Polymeric materials have usually been utilized as insulators. Electroactive polymers (EAPs), a new class of materials, have challenged this perception. EAPs are receiving increased attention from academia and industry because they have a wide variety of applications such as biosensors, artificial muscles, actuators, corrosion protection, electronic shielding, environmentally sensitive membranes, visual displays, solar materials and components in high energy batteries. The commercialization of EAPs, however, has not been realized to any great extent due to limitations in production and mechanical properties. Biobased polymers or biopolymers have unique physicochemical properties that make them attractive for use as EAPs. The best example of functional polymers can be found in nature where well-defined macromolecules and architectures assemble into complicated natural systems. Inspired by the potential of biomacromolecules, we are

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pursuing the design of tailored, functional polymeric materials using physical and chemical methods for use as electroactive biopolymers.

## Electroactive Polymers

The first polymer shown to conduct electricity was poly(acetylene).[1] The 2000 Nobel Prize in Chemistry* was shared between chemist Alan MacDiarmid (USA & New Zealand), physicist Alan Heeger (USA) and chemist Hideki Shirakawa (Japan) based on the discovery of conductive organic polymers. Since conducting polyacetylene was discovered, a number of other conducting polymers with unique properties have been developed. Electroactive polymers are usually classified into two categories, conducting polymers and polymer electrolytes, depending on the mode of electron transport. Conducting polymers are electronic conductors by virtue of $\pi$ electrons via conjugated double bonds and are referred to as intrinsically conducting polymers (ICPs). Morphology & physical properties depend on growth conditions for synthetic ICPs. Once formed, synthetic ICPs are disordered so that their structure does not form a well-ordered architecture, resulting in undesirable physical properties. Some examples of popular synthetic ICPs are poly(thiophene), poly(aniline), and poly(pyrrole). Polymer electrolytes achieve their functional conductance by ion-conduction. Different salts may be dissolved into the solid polymer (usually with a small amount of solvent) creating a solid polymer electrolyte (SPE). The dissociated ions are free to move within the matrix and can conduct electricity under applied voltage just as they do in conventional solutions.

## Thermoplastic Starch as an Electroactive Biopolymer

Starch is a biodegradable, renewable resource. While starch is packaged into granules in its native state (Figure 1a), the properties of starch materials are exhibited when the granular structure is broken down by mechanical and thermal means. Starch is composed of a mixture of linear and branched polysaccharides (Figure 1b). Amylose is a linear polymer of (1,4) linked anhydroglucose units (AGU). Amylopectin is a highly branched polysaccharide composed of linear (1,4) AGU chains with branch points having (1,6) linkages between amylose chains. Starch obtains its plastic properties upon the gelatinization and destructuring of starch granules with enough water and

* http://www.nobel.se/chemistry/laureates/2000/

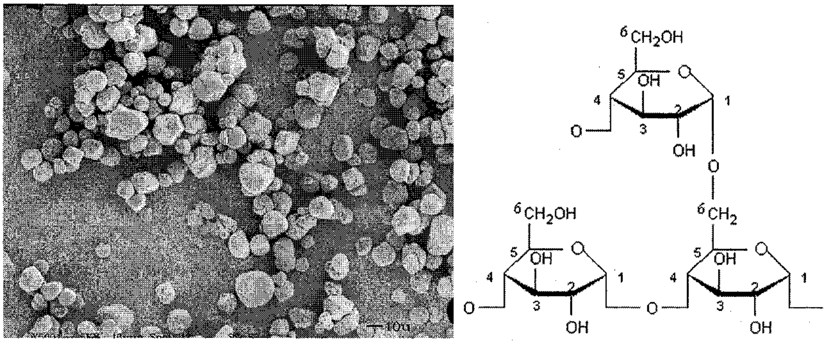

Figure 1: (a) SEM of native starch granules. (b) The chemical structure of amylose and amylopectin.

thermomechanical energy. Starch can be gelatinized by benchtop heating of a water dispersion or cold gelatinized with NaOH, but true thermoplastic starch (TPS) is easily obtainable through extrusion. The moisture content is usually 30% compared to 95% for casting films of polysaccharide solutions. Utilizing reactive extrusion, TPS can be derivatized, blended with salts to produce ionic conductors, or blended with small amounts of ICPs in a single, continuous process.

A direct-current resistance technique was used to measure resistance in polysaccharide films.[2] This test method involves a direct-current procedure for surface and volume resistance/resistivity of powders, pellets and thin sheets and conforms to the standards established by ESD S11.11 and ASTM D257 (American Society of Testing Materials, 1993). Resistance is directly measured using a defined electrode configuration (concentric ring electrode), specific test voltage (0.75 V) and controlled environmental conditions. Samples were stored in 50% RH and standard room temperature (23°C).

Starch-based materials are moisture sensitive and will absorb/desorb moisture from the atmosphere, and the amount of moisture in the system will affect the polymer and ion mobility within the system as well as the quality of physical properties of TPS.[2] While moisture contributes to the overall bulk conductance of TPS, it does not at or above MCs of about 25-30% (Figure 2). Therefore, the effect of metal halides (MX) on physical properties and electroactivity was determined by keeping moisture content (and plasticizer content) constant. TPS, produced by reactive extrusion,

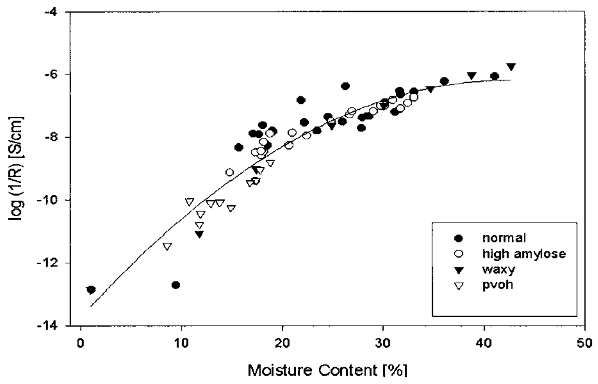


Figure 2. Contribution of water to the conductance of thermoplastic starches.

was doped with MX.[3,4] The concentration of MX was kept on a molar basis to AGU rather than weight basis so that the effect of charge species could be examined. TPS with 20% moisture exhibits a conductance of $10^{-9}$ to $10^{-11}$ S/cm as measured by direct current methods. Starch is naturally insulative, and its proton mobility is low.[5] Upon doping with metal halides (NaCl, NaI, LiCl, and LiI), the material exhibited conductance between $10^{-5}$ to $10^{-6}$ S/cm. At the same molar ratio, different mixtures of TPS-MX would exhibit different levels of conductance (Figure 3a). The addition of MX affected the mechanical properties of TPS. In general, the films became more flexible as the amount of MX increased probably due to the plasticizing effect of large anions.[6] Starch-based solid polymer electrolytes exhibit increased electrical conductance with increasing $M^+X^-$ content. Greater polymer mobility is exhibited, represented by elongation (Figure 3b). Polymer mobility plays an important role in ion-conducting polymers by facilitating ion dissociation and ion mobility.

Starch can be derivatized to add functionality to electroactive biopolymers. Other natural polysaccharides have anionic and cationic functional groups that affect the ion-conductivity of resulting biomaterials. Water-soluble polysaccharides are excellent film formers for use as coatings or laminates rather than for matrices as proposed for starch.

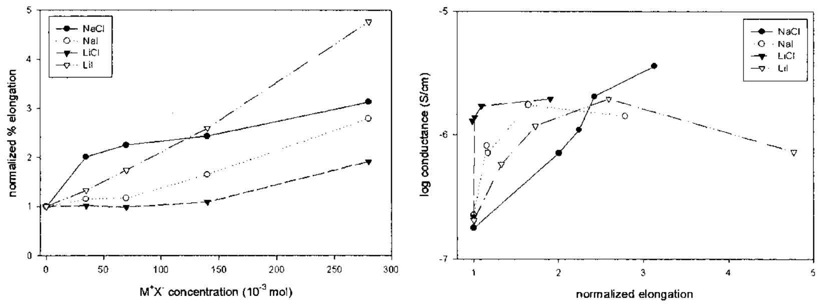


Figure 3. Starch-based solid polymer electrolytes with different metal halides exhibit (a) greater polymer mobility expressed by elongation for the same concentration, and (b) different conductance based on ion mobility and polymer mobility.

## Conclusions

Starch-based electroactive biomaterials are solid polymer electrolytes utilizing ion mobility as the primary mode of conduction within the polymer matrix. Biopolymers (biopolymers) offer a degree of functionality not available in most synthetic ICPs. Biopolymers are a renewable resource and have a wide range of uses. Agriculture-based biopolymers could also have an economic advantage over synthetic, petroleum-based products in the future.

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